DEVELOPMENT OF A SOLID STATE COULISTER

Final Report
to the
Department of Army
Harry Diamond Laboratories
Washington D. C. 20438

Author: S. Giles

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Date: 30 January to 1 August 1968

Atomics International
a Division of North American Rockwell Corporation

34

ABSTRACT

The development program conducted under this contract has resulted in a coulister (electrochemical timing device) which not only meets the performance requirements of the contract but exceeds the desired performance. It appears that the next phase should be one of developing mass production techniques and quality assurance performance data on large quantities of devices.

Required Performance		Demonstrated Performance
-55°C to +71°C	Temp. Range	-62°C to +93°C
Less than 0.1 cu.in.	Volume	0.025 cu.in.
3 to 1500 μA-sec	Operating Time	3 to 2000 μA-sec
10 to 100 μA	Operating Current	1 to 1500 μA
0.5 second or less	Rise Time	0.2 to 0.5 seconds
± 5% reqd. ± 2 1/2% desired	Accuracy	Less than ± 2 1/2%

INTRODUCTION

Military fuze time delay functions have been controlled by mechanical and chemical devices for many years. These systems have limited accuracy due to the influence of ambient temperature and are difficult to protect against high shock loads. The development of solid state electronic circuits has significantly reduced the size of timing devices. The discovery of a solid state electrolyte has made it possible to develop an electrochemical timer which will perform over the MIL spec range of -65F to +165F. The advantages of this system were recognized by H. D. L. and the results of the Army funded development program are reported herein.

An electrochemical coulister consists of a source of plateable metal, an electrolyte, and a substrate. The coulister is set by applying a known current for a controlled period of time, thus plating the desired amount of metal on the substrate. When a controlled current is applied through the device in the opposite direction, the plating material is stripped from the substrate. When all the metal has been removed, the resistance of the device suddenly rises. This change in resistance can be sensed by a suitable external electronic circuit and the desired end-of-time function initiated. The coulister current may be varied or pulsed during operation to provide various lengths of operating time. The amount of metal plated can also be varied. The current-time operating function is within a few percent of the current-time setting cycle. As can be seen by the data in the attached report, accuracy of better than ±2% has been obtained.

The projected cost, mechanical strength, the compactness, and the wide temperature operating range of coulisters developed under this program make them ideal for fuze timing functions. In fact, it appears that the solid state coulister is more resistant to environmental stress than the other fuze circuitry components.

The work under this contract was for analyzing operation of the coulister in the 5 to 150 second time function range. It appears that the same device, with minor modifications, can be developed to provide controlled delay functions of up to a month or more.

INDEX

FIGURES

I. OBJECTIVES AND RESULTS

The objective of the program was to design, fabricate and evaluate a solid-state timer (coulister) for use in artillery fuzes. The following discussion outlines the performance characteristics required and the results discussed:

A. Environmental

Operating Temperature Range:	$-65^{\circ}F$ to $+165^{\circ}F$ desired, $-40^{\circ}F$ to $165^{\circ}F$ required. $-100^{\circ}F$ to $200^{\circ}F$ has been demonstrated.
Storage:	Devices stored at the desired temperature range for periods of days showed no degradation ($-65^{\circ}F$ to $+165^{\circ}F$).
Dynamic:	30,000 g's for several milliseconds - survive and operate up to 35,000 rpm during time out. No tests conducted under this contract, but no theoretical reason why this device will not perform.
Shelf Life:	10 years desired: Measurement of impurity currents indicates no degradation with time. No self-setting indicated during storage.

B. Configuration

Body:	No dimension should exceed 1" (leads not included). Figure 1 shows the 1/4" diameter by 1/2" long body.
Volume:	Less than 0.1 cubic inch desired. Actual size $\sim$0.025 cubic inch.
Leads:	Two nickel wire, solderable and rugged enough for handling and potting.

NO. Figure 1

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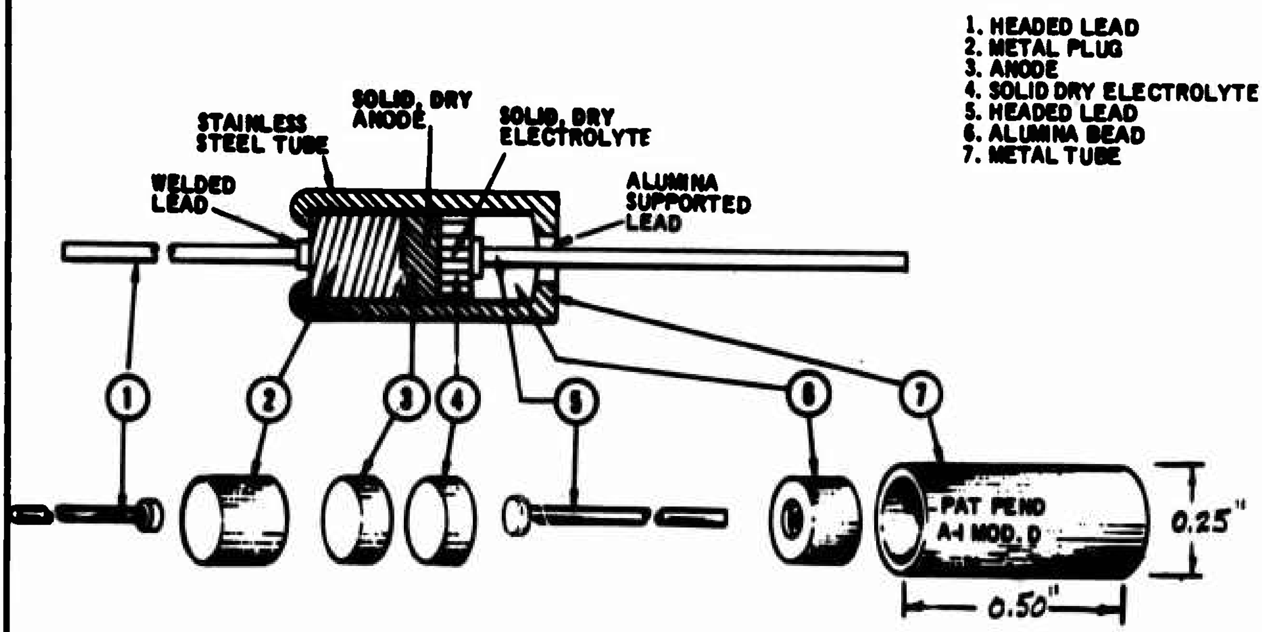


CUT-AWAY DIAGRAM OF AN AI SET CELL

*Pat. Pending

C. Performance

Run Condition:	Requirement was 10 μA to 100 μA. Tests were conducted to determine the optimum running (time out) current for maximum efficiency (accuracy). It appears that this current can be between 3.0 μA and 1500 μA. The device operates satisfactorily at 1.0 μA.
Time Out:	The voltage drop across the coulister shall be less than 0.1 volts. The enclosed data plot shows that this requirement is met up to 100 μA time out current level.
R se T me:	The elapsed time between 0.1 and 0.6 volts at end of time out should be and was found to be 0.5 seconds or less.
Set Time and Voltage	The coulister shall be capable of being set in less than 1 second at less than 0.3 volts. This requirement is met under all conditions except at and below -65°F when voltage is between 0.3 and 0.4 at 1.5 mA. See Figure 14.
Setting Charge:	It is desirable to have the applied setting charge within 5% of the applied time out charge. In terms of "efficiency" the setting vs time out efficiency development objective is 95% to 100%. This requirement was met; set "Accuracy."
Clearing	The coulister should be capable of being cleared (accelerated operation) in less than 1 second after being set up to 1500 μA-seconds. This was demonstrated.

Accuracy: The efficiency or repeatability of the coulister timing device is the key requirement. A time out or operating accuracy of ± 5% is required and ± 2 1/2% is highly desirable. This is defined as the ratio of operating μA-second to set μA-seconds. The tests were conducted with a 21% electronic analyzing system for setting and operating the timers. The data reported herein indicates that the requirement has been met and that the desired ± 2 1/2% may be accomplished.

D. Cost

The program objective included cost and production analysis aimed at a mass produced device with low cost for general purpose applications. The simplicity of the device indicates that volume production will result in low cost devices.

II. TEST PROCEDURE

Evaluation of the devices was conducted during the program by testing with the following procedure and instrumentation:

A. The timer leads are identified as follows, regardless of current flow direction:

1. The lead welded to the outside sleeve shall be defined as the "cathode."

2. The center lead (plating substrate) shall be defined as the "anode."

B. An a-c ohm meter was used for all resistance measurements.

C. The terms "set" and "operate" are used to describe the cycling of the device, "set" meaning transferring active metal anode material from the sleeve lead (cathode) to the center lead (anode); "operating" or timing out meaning returning the metal to its source, i.e. cathode.

D. Unless otherwise indicated, timing tests were conducted as follows: timer setting current was 1500 μA or less for 1 second, and time out current varied from 1 μA to 1500 μA. (Short time outs are run by lowering set current, shortening set time or raising time out current.)

E. Timer cut-off voltage was set at 600 mV for most tests, although a limited number of tests were conducted to measure the "stop" or maximum voltage at the end of operation.

F. Prepared data sheets were used for all data recording the following:

1. Test Temperature
2. Set Rate
3. Set Time
4. Set Voltage
5. Operating Rate
6. Expected Time Out
7. Actual Time Out
8. Rise Time (.1V to .6V)
9. Accuracy

G. Setting and operating voltage characteristics were recorded on an x-y recorder or an oscilloscope. Each trace was identified with device serial number and test temperature. Any significant variation, such as the inability of a timer to reach cut-off voltage, loose contact, etc. was recorded.

H. Initial Operation Following Assembly

1. Connect the timer electrically to the test panel.

2. Operate the device at the desired current, measure and record all parameters. This is to strip any residual set.

I. Ambient Test (Room Temperature)

1. Connect the timer electrically to the test panel. Set cut-off voltage at 600 mV.

2. Set timer (typically 1500 μA for 1 second), measure and record temperature, set rate, set time, set voltage, and expected time out.

3. Operate the timer at the desired current, measure and record time out rate, actual time out, rise time and accuracy.

4. Repeat steps 2 and 3 at least once to varify results.

J. High and Low Temperature Tests

1. Place timer in an environmental chamber capable of maintaining desired temperature.

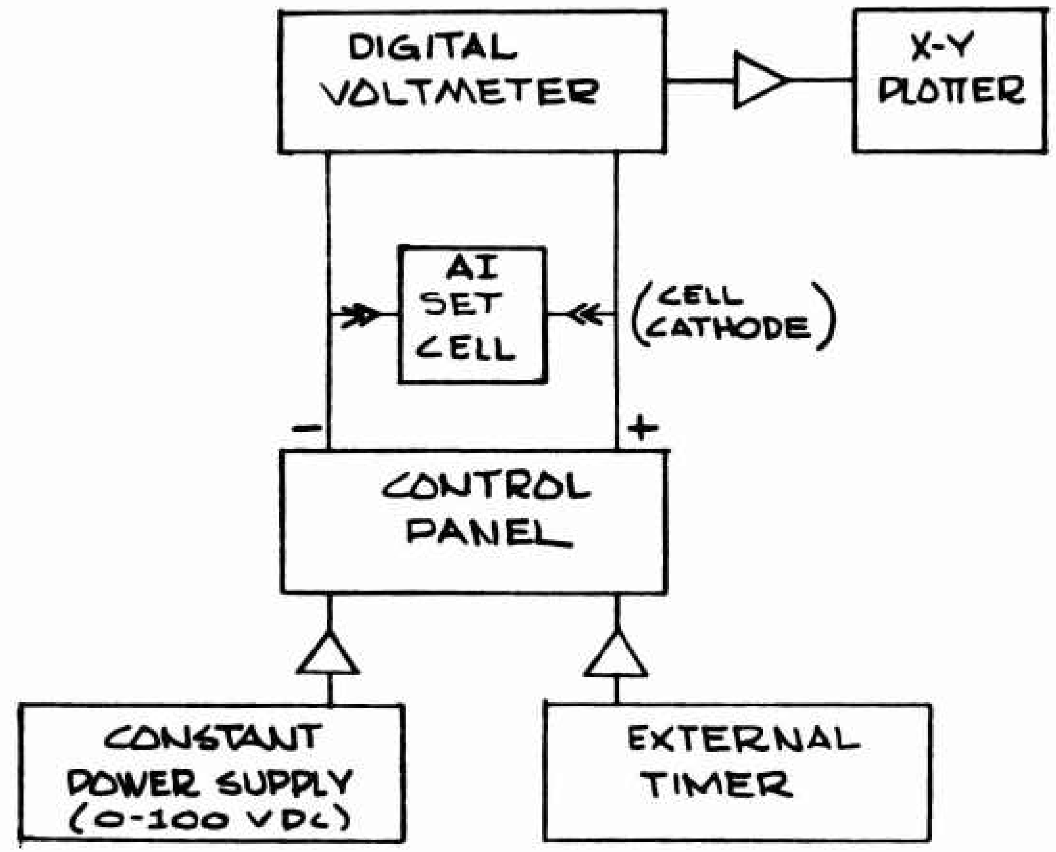
2. Connect the timer electrically to the test panel. Set cut-off voltage at 600 mV.

3. Set environmental temperature control to desired temperature. Allow 10 minutes stabilization after chamber has reached control point.

4. First clear by timing out at 10 μA, then repeat steps 2, 3 and 4, Section B.

The attached block diagrams illustrate the equipment used to set and operate the timers.

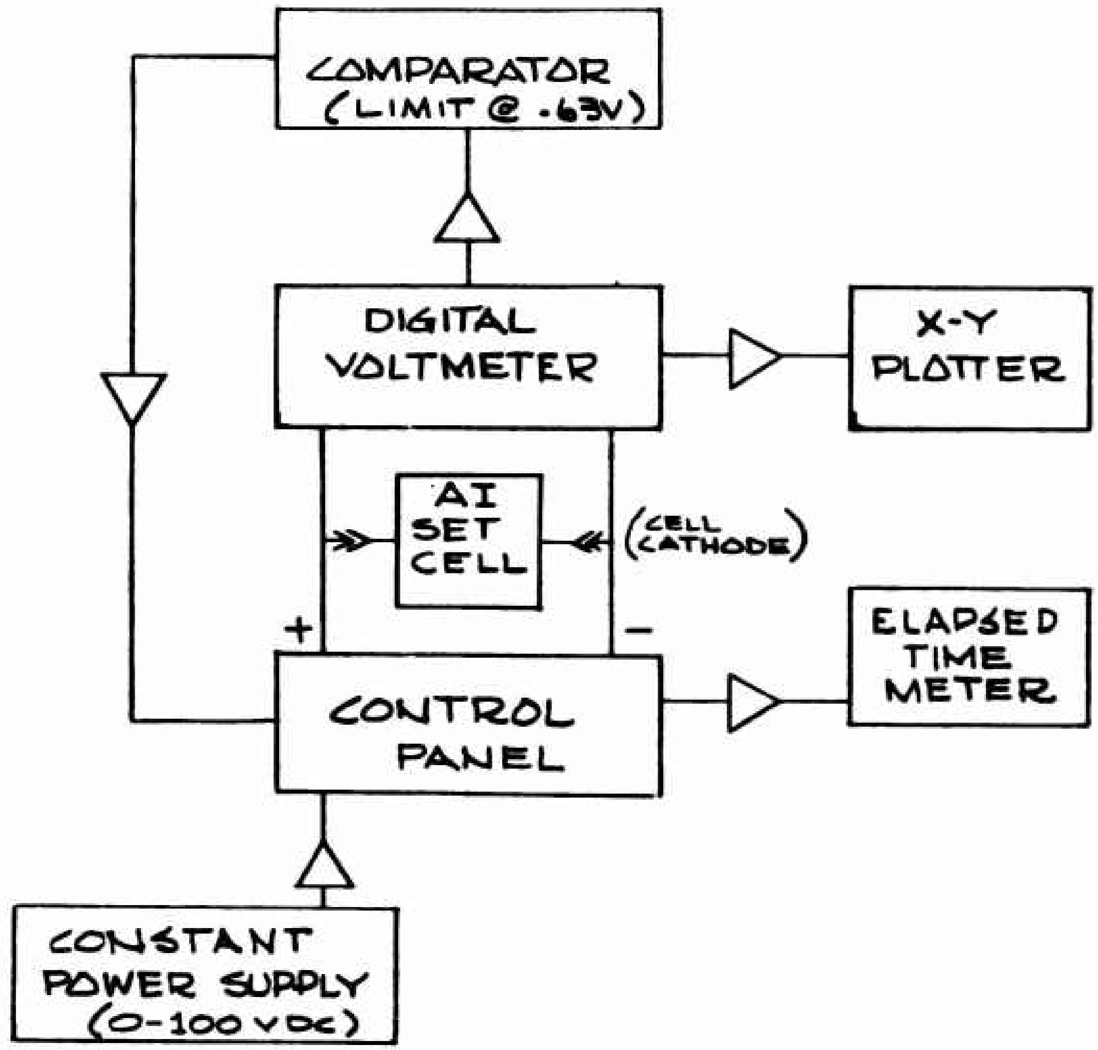
Figure 2 shows the equipment necessary for setting the timers. Figure 3 shows the operating or time out equipment. Figure 4 combines the equipment for both operations into one system.



ATOMICS INTERNATIONAL
"SET" BLOCK DIAGRAM

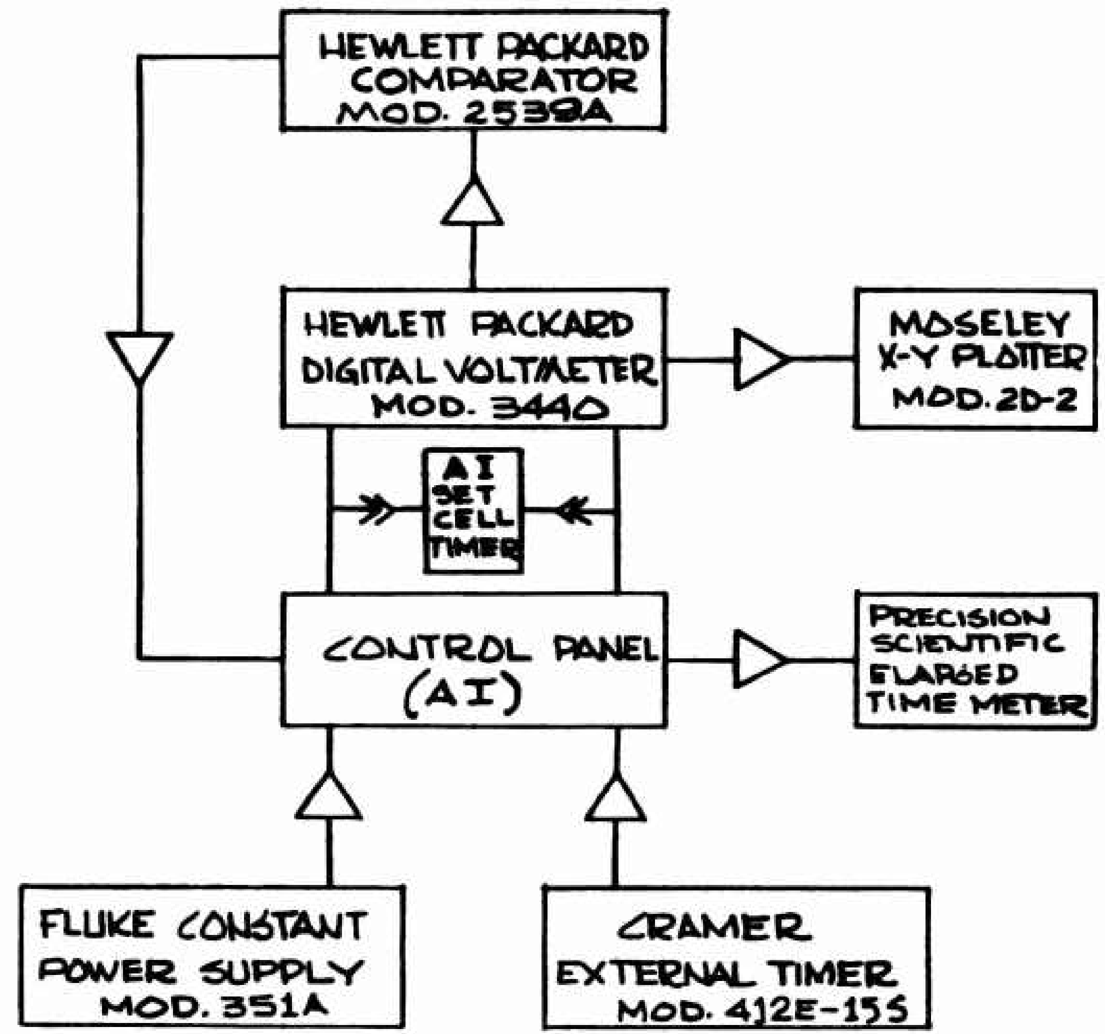
FIG. 2

5/23/67
MMT



ATOMICS INTERNATIONAL
"TIME~OUT" BLOCK
DIAGRAM
FIG 3

5/23/67
MMT



ATOMICS INTERNATIONAL
SET & TIME OUT BLOCK DIAGRAM

FIG. 4

NOTE; AI CONTROL PANEL IS A SET-CELL POLARITY REVERSING CIRCUIT & ELECTRICALLY REMOVES THE SET-CELL AT END OF TIME-OUT (.63V)

5/23/67' M/AT

III. TEST DATA

The program was started with a set of prototypes which had been fabricated three months before receipt of this development contract. New sets of prototypes were fabricated as tests and analysis revealed possible improvements.

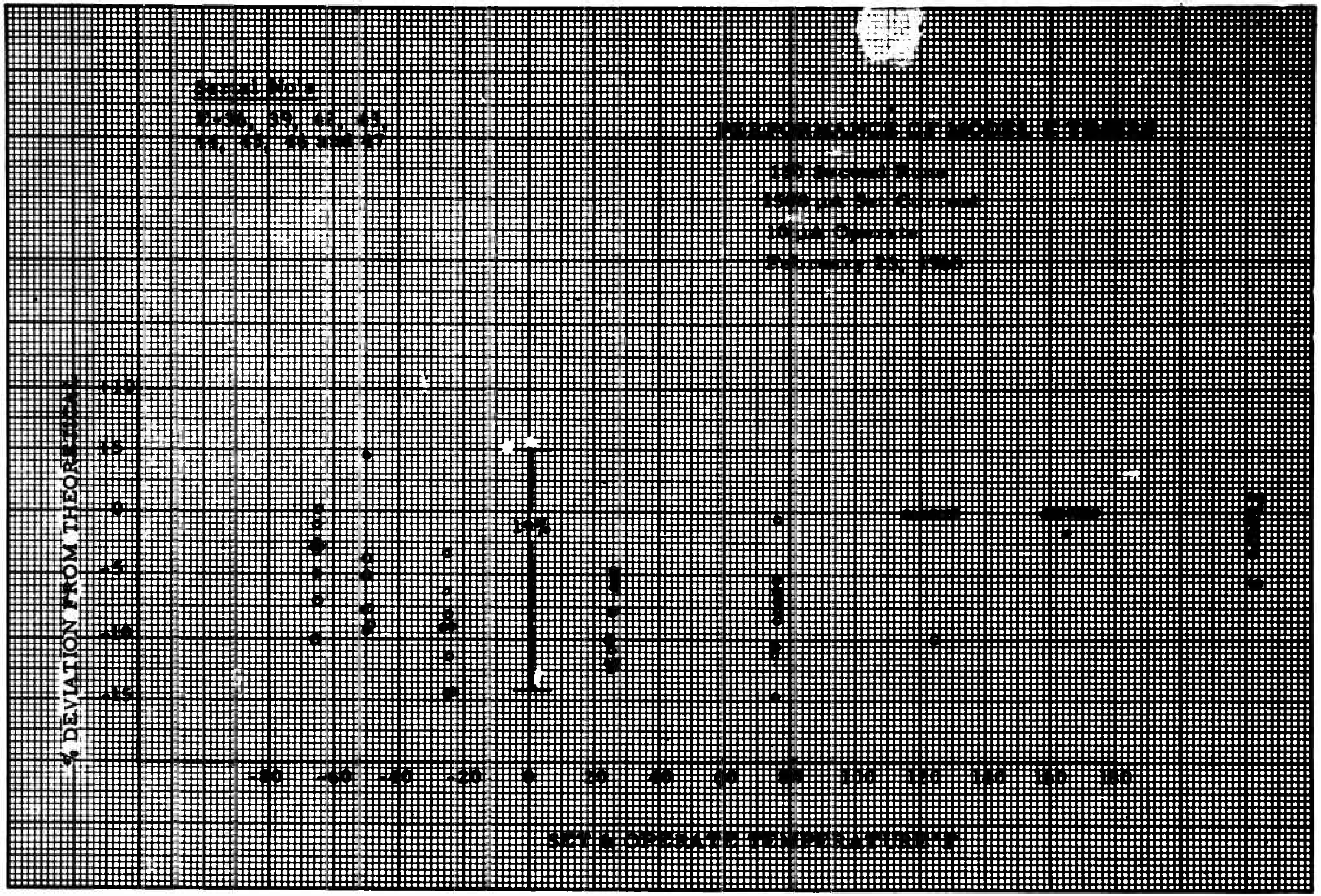
A. The first group of timers tested revealed that that the desired accuracy was not provided. Analysis of the data and the devices indicated that improvement of the fabrication techniques would provide more accurate devices.

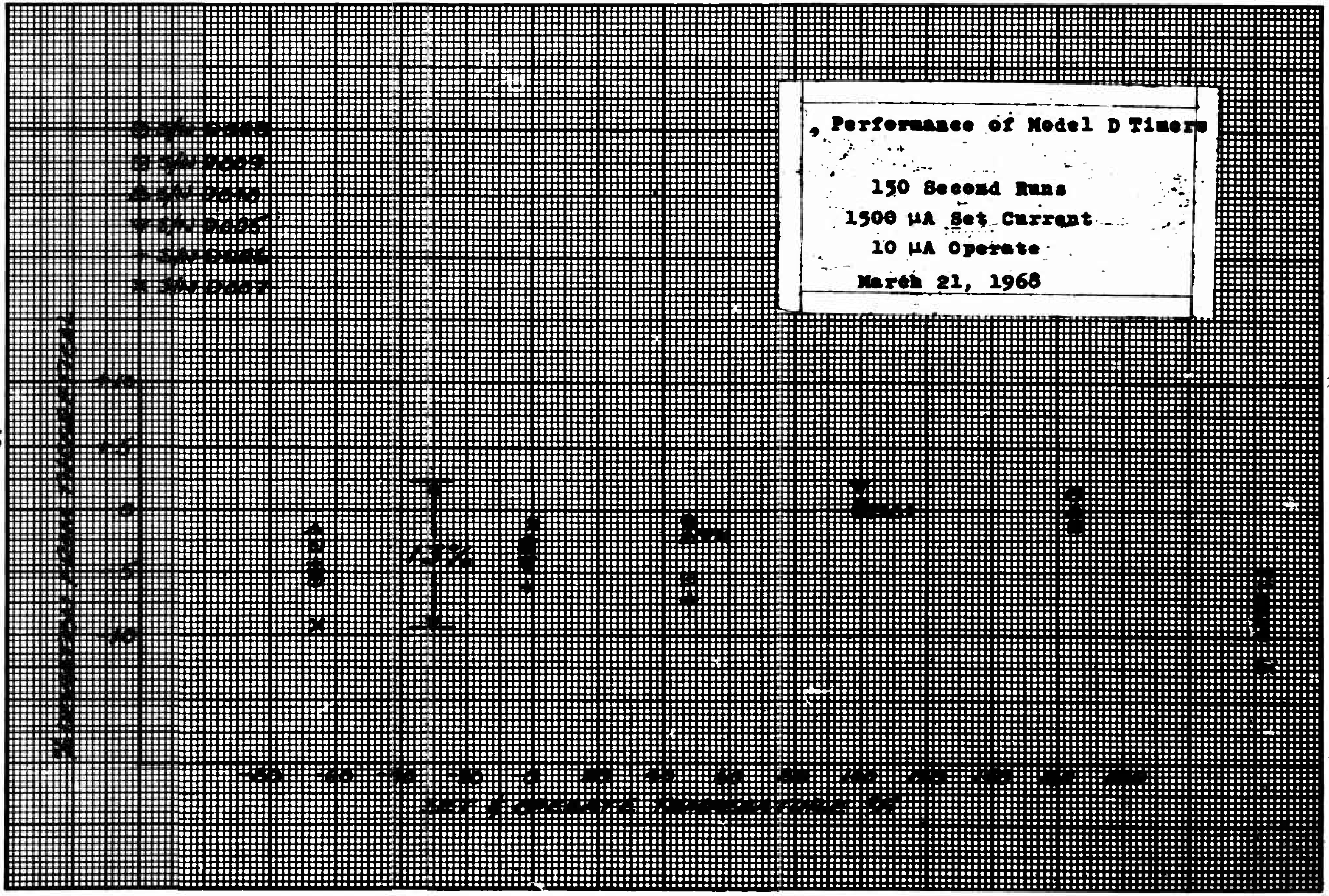
The plot of accuracy of eight timers, set and operated at various temperatures, is shown in Figure 5. The poor performance (85% to 105%) at low temperatures shows that compensation for differential expansion was not provided. New tooling and alumina insulators were designed and procured, more timers fabricated and tested.

B. Test data for the second set of improved prototype timers revealed that the set current and rise time voltage characteristics were not accurately reporduced by the x-y recorder. An oscilloscope with camera was added to the data system to more accurately record these variables.

Performance tests of this set of prototypes were conducted over the -65°F to +165°F temperature range. Evaluation of the initial data revealed that some minor improvements of the assembly procedure used on the first few prototypes would improve the performance of the timer. The reported data are therefore for the second half of each group; S/N D005 through D010 and S/N D018 through D021. The improved technique is reflected by the improved performance.

Figure 6 summarizes the results of setting and operating six prototype timers at -65, 0, 50, 100 and 165°F. The data are plotted in % deviation from theoretical time out. The timers were set by applying a current of 1500 μA for 1 second with the cathode positive.


% DEVIATION FROM THEORETICAL
+10
+5
0
-5
-10
-15
-80
-60
-40
-20
0
20
40
60
80
100
120
140
160
180


Performance of Model D Timers
150 Second Runs
1500 µA Set Current
10 µA Operate
March 21, 1968
±3%

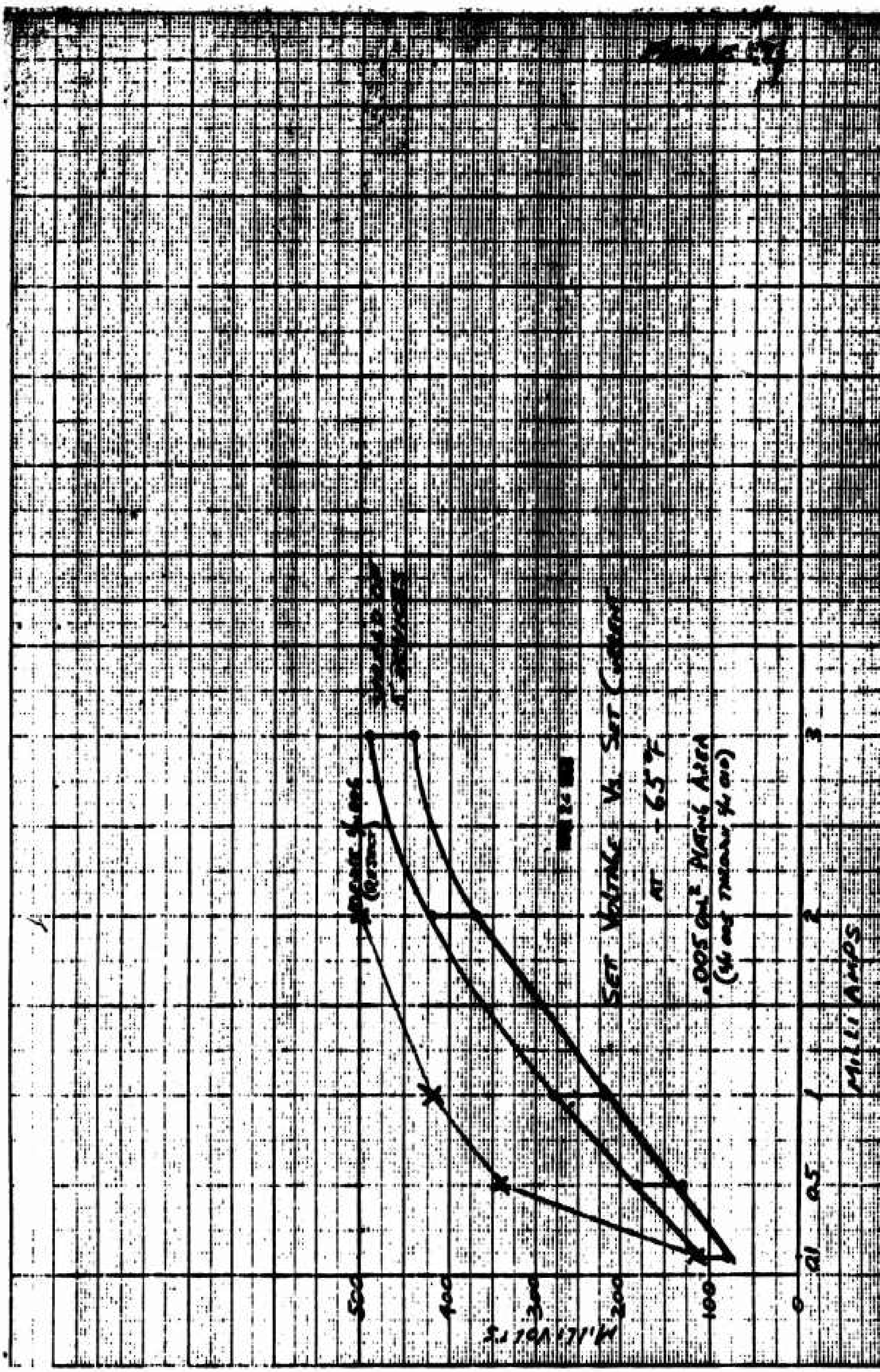
This ratio of setting to operating current was selected for convenience. Other currents may be used to provide different time cycles.

At low temperature, the data plotted in Figure 6 shows a negative 9% deviation from theoretical in one test. At high temperature there appears to be less deviation. The data plotted in Figure 7, 8, and 9 indicates that the resistance of five of the six devices are within the desired range and the variation between devices is reasonable. One device, D006, shows consistently higher resistance than the other five. This appears to indicate faulty assembly. This pattern was confirmed by later prototypes and appears to be a good quality control technique. The intial voltage check requires only a second or two and can be employed to operate a reject station in an automated assembly line.

C. The third group of four timers (S/N D018, 019, 020 and 021) fabricated and tested showed improved performance. In fact, the deviation from theoretical operating time was so slight that the setting and operating current control equipment may produce a significant part of the error.

Photos 1, 2, 3, 4, 5 and 6 in Figures 10 and 11 show the timer voltage rise at the end of the 150 second operation recorded on the oscilloscope. These are typical performance characteristics for this group of prototypes over the temperature range. They show that the voltage change occurs in 0.5 second or less. The sudden drop in voltage is produced by the automatic cut-out circuit in the test equipment. This cut-out is set a 0.6 volts but does not react quickly enough to prevent the timer from momentarily reaching 0.68. There is not degradation caused by such short exposure to over-voltage condition. The rise time indicated by these traces is very close to theoretical.

Figure 12 summarizes the deviation of these four devices when set and timed out over the desired temperature range. The variation of the group was from 95% to 100.6% of theoretical time out.


SET VOLTAGE VS. SET CURRENT
AT -65°F
MILLIVOLTS
MILLIAMPS
500
400
300
200
100
0
.1
.5
1
2
3

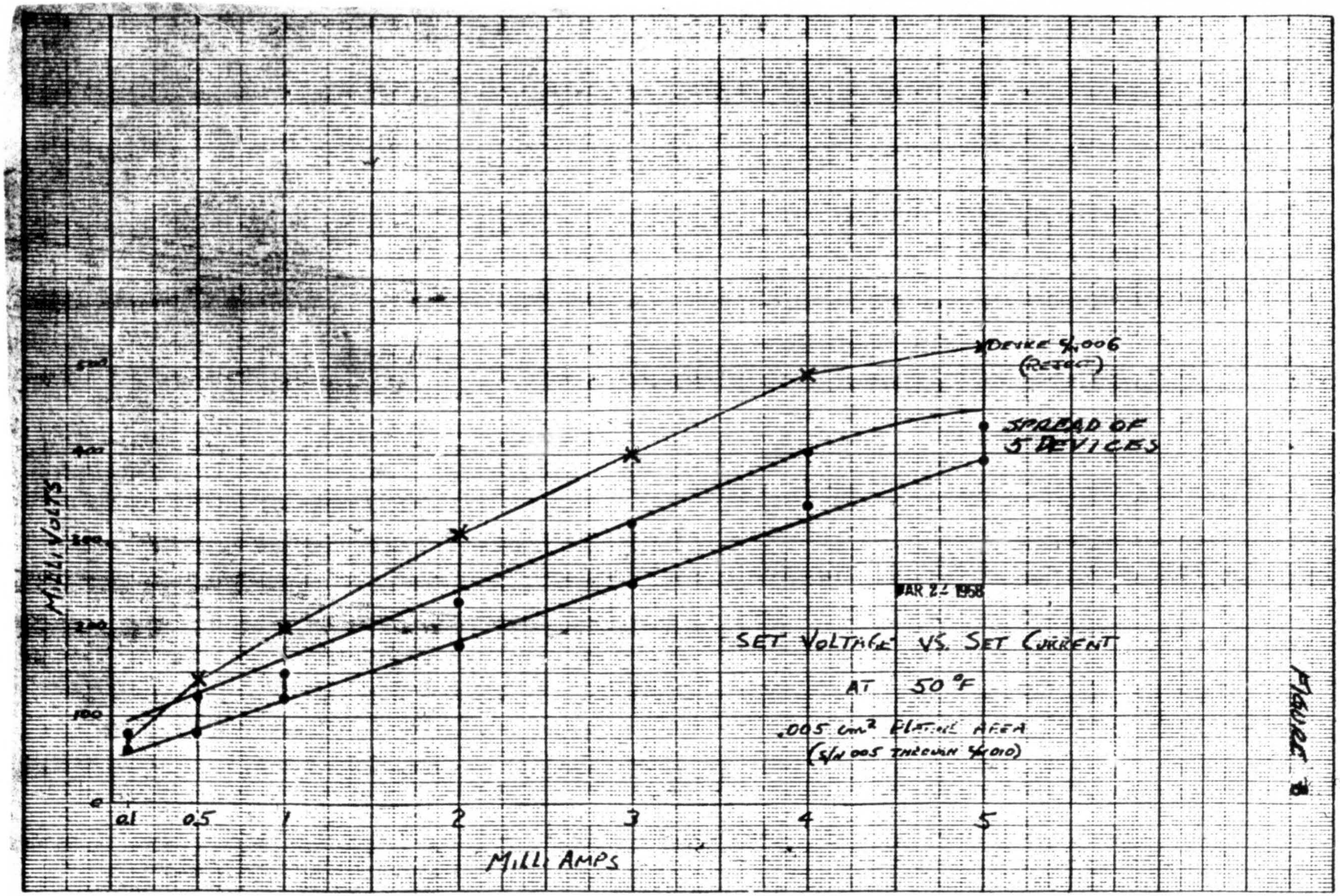


FIGURE 8
DEVICE S/N 006
(REJECT)
SPREAD OF
5 DEVICES
MAR 22 1958
SET VOLTAGE VS. SET CURRENT
AT 50 °F
.005 cm² PLATINE AREA
(S/N 005 THROUGH S/N 010)
MILLI VOLTS
MILLI AMPS
0
100
400
500
.01
0.5
1
2
3
4
5

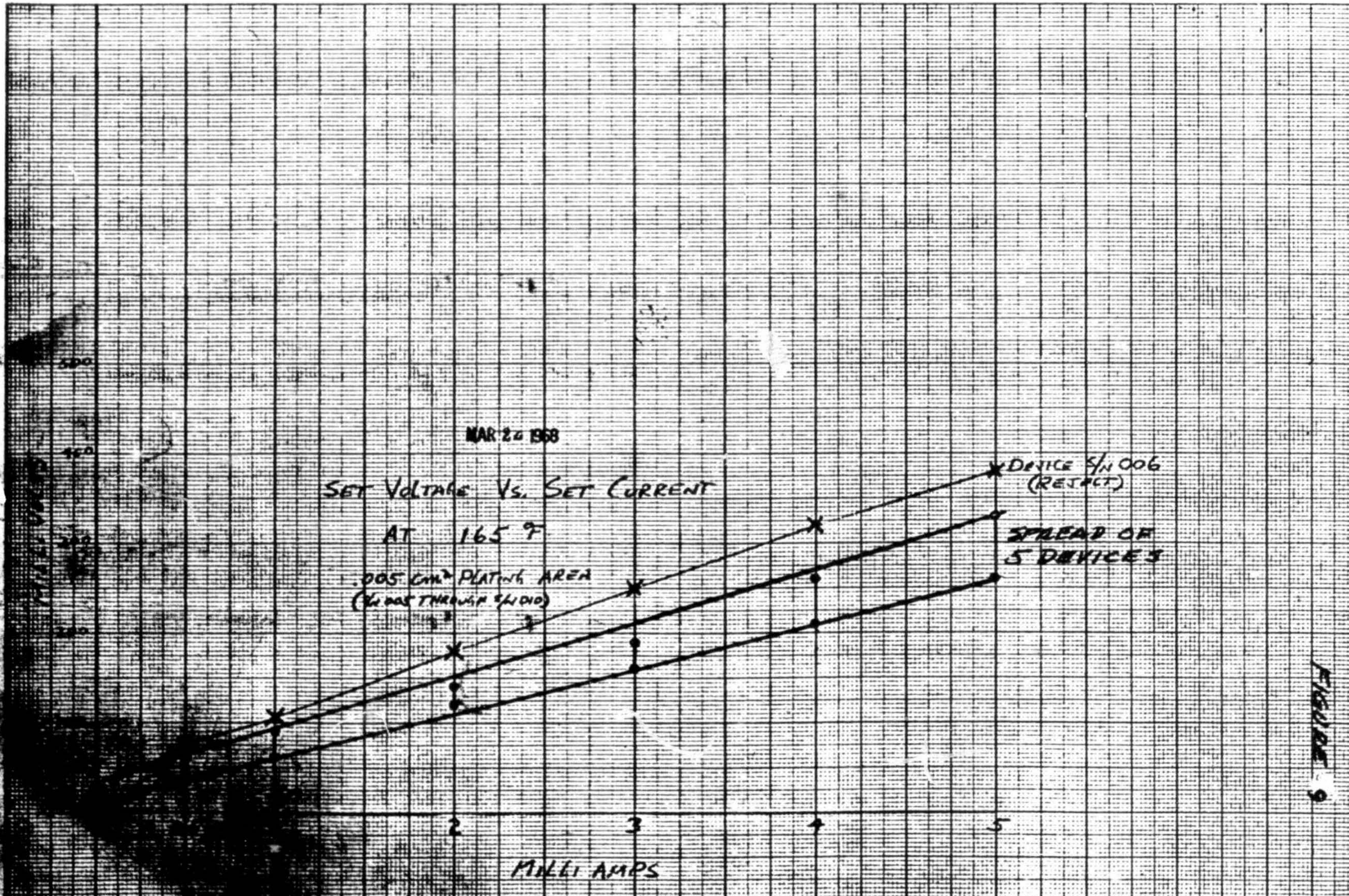
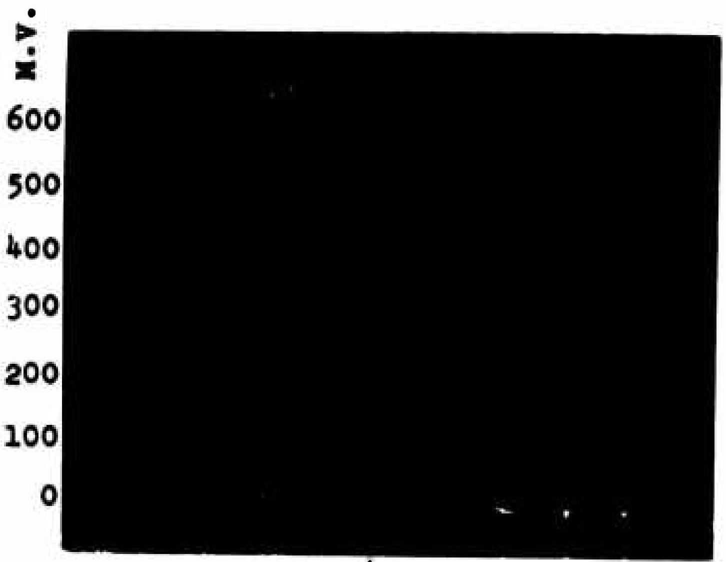

MAR 26 1968
SET VOLTAGE VS. SET CURRENT
AT 165 °F
.005 CM² PLATING AREA
DEVICE S/N 006
(REJECT)
SPREAD OF
5 DEVICES
2
3
4
5
MILLI AMPS

FIGURE 9

P.R.DuBois
3-29-68

Figure 10

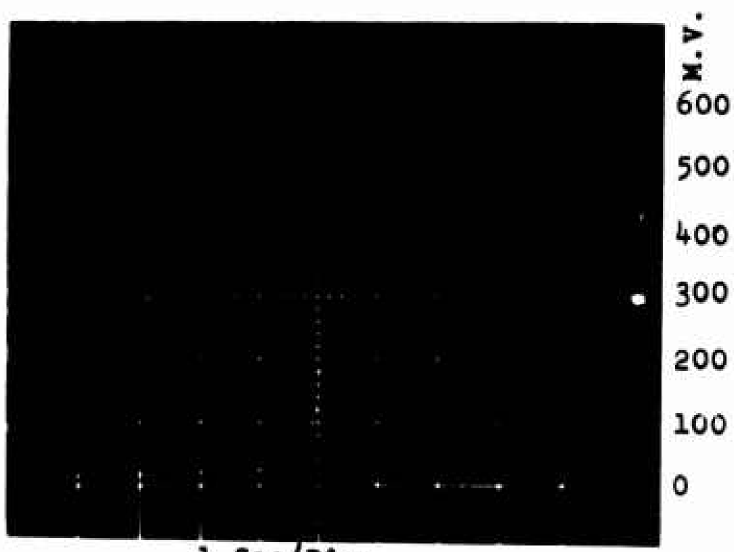
Photo 1



1 Sec./Div.

100°F

Photo 2



1 Sec/Div.

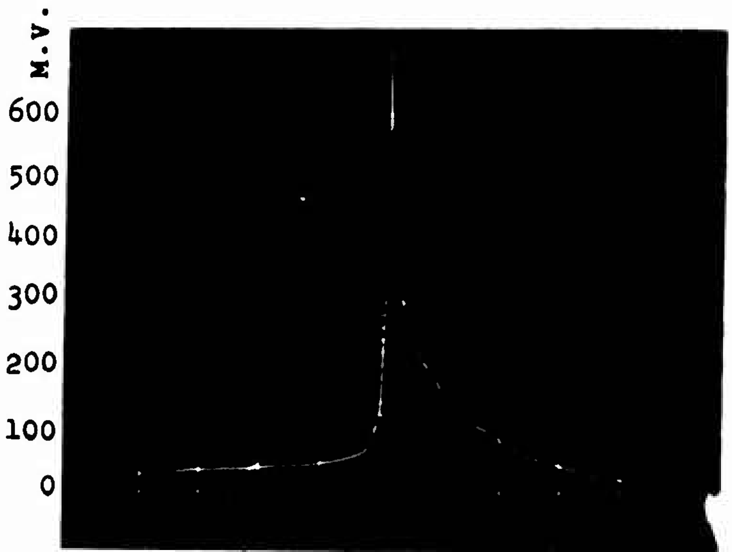
165°F

Last Seconds of Typical
Model "D" 150 Second Timeout

Figure 11

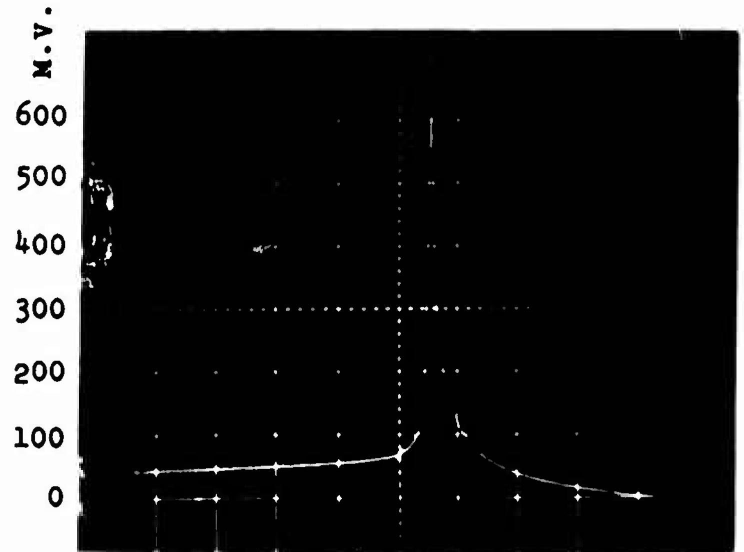
P.R.DuBois
3-29-68

Photo 3



1 Sec./Div.
$0^{o}F$

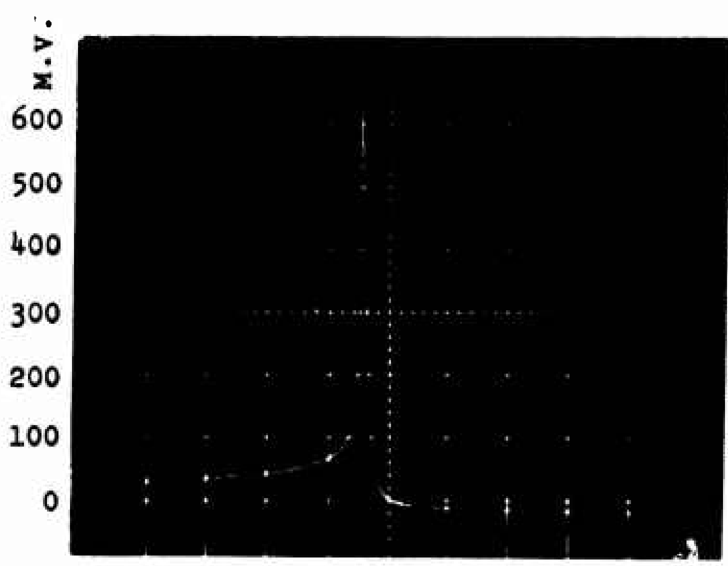
Photo 4



1 Sec./Div.
$-65^{o}F$

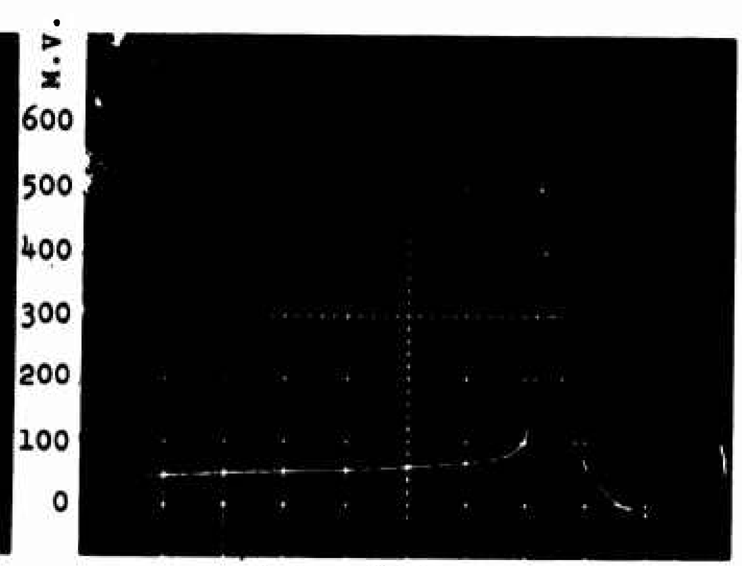
Typical Timeout Trace of
Model "D" Timers

Photo 5



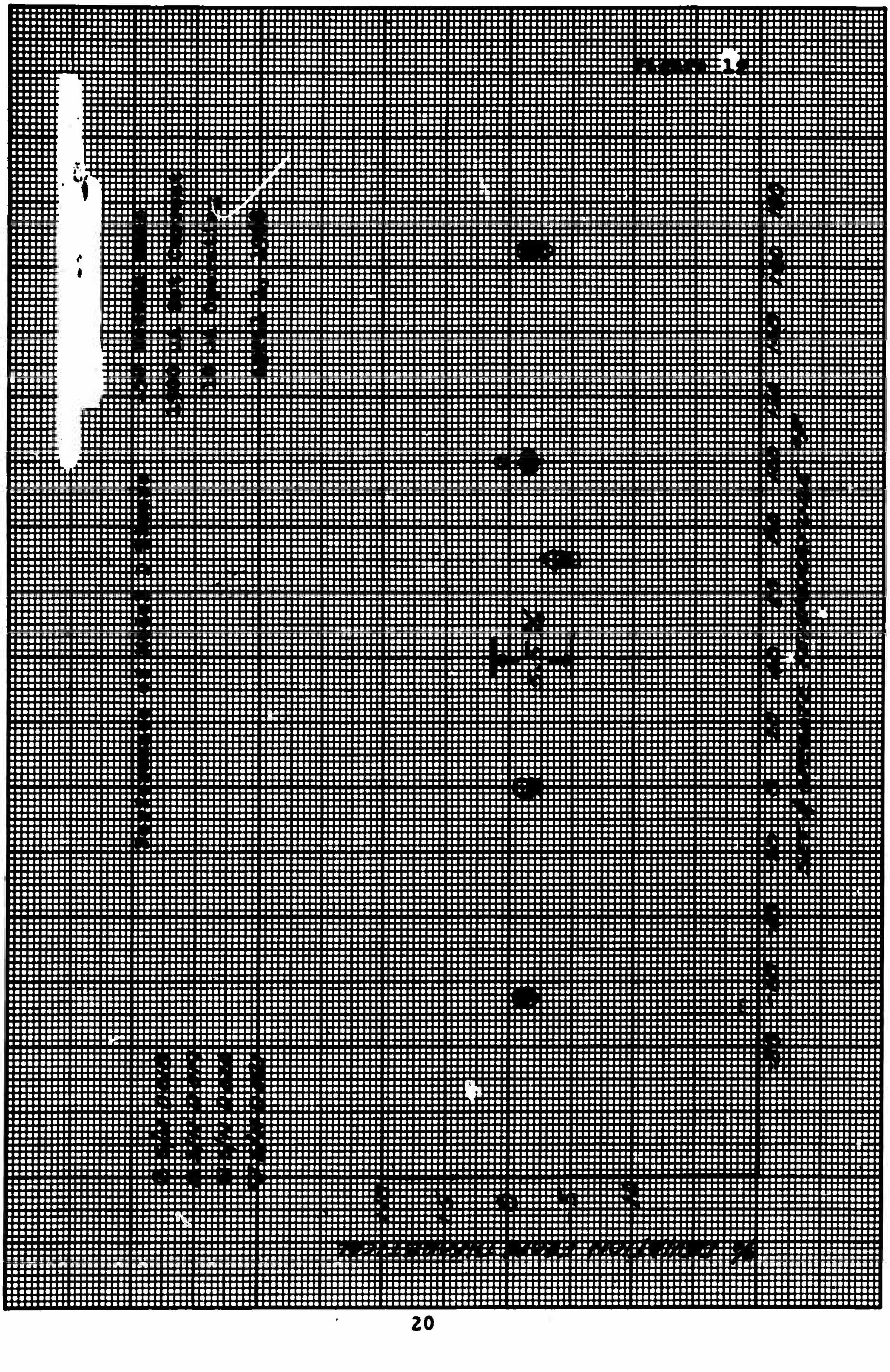
1 Sec./Div.
$0^{o}F$

Photo 6



1 Sec./Div.
$-65^{o}F$

Typical Timeout Trace of
Model "D" Timers



A review of the data revealed that some of the devices performed within very close tolerance over the temperature range:

Serial No.	Time Out Spread Sec.	Rise Time Sec.
018	157 - 144 = 13	2.0
020	149 - 143 = 6	2.0
019	147 - 149 = 2	0.6
021	144 - 148 = 4	0.4

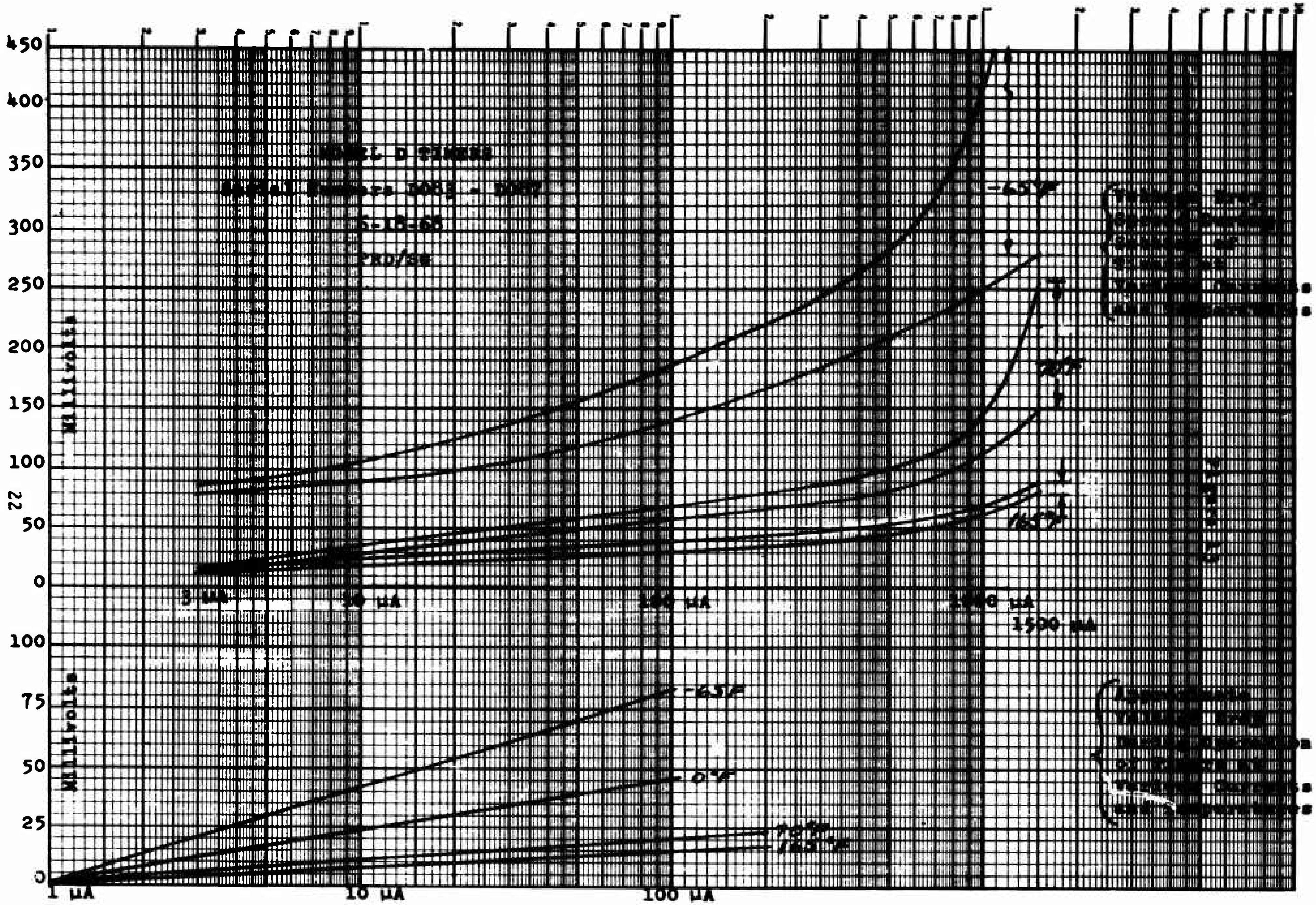
This very small sample suggests the possibility of selectively grading devices by measuring rise time. More statistics must be collected before this can be used as a performance criteria.

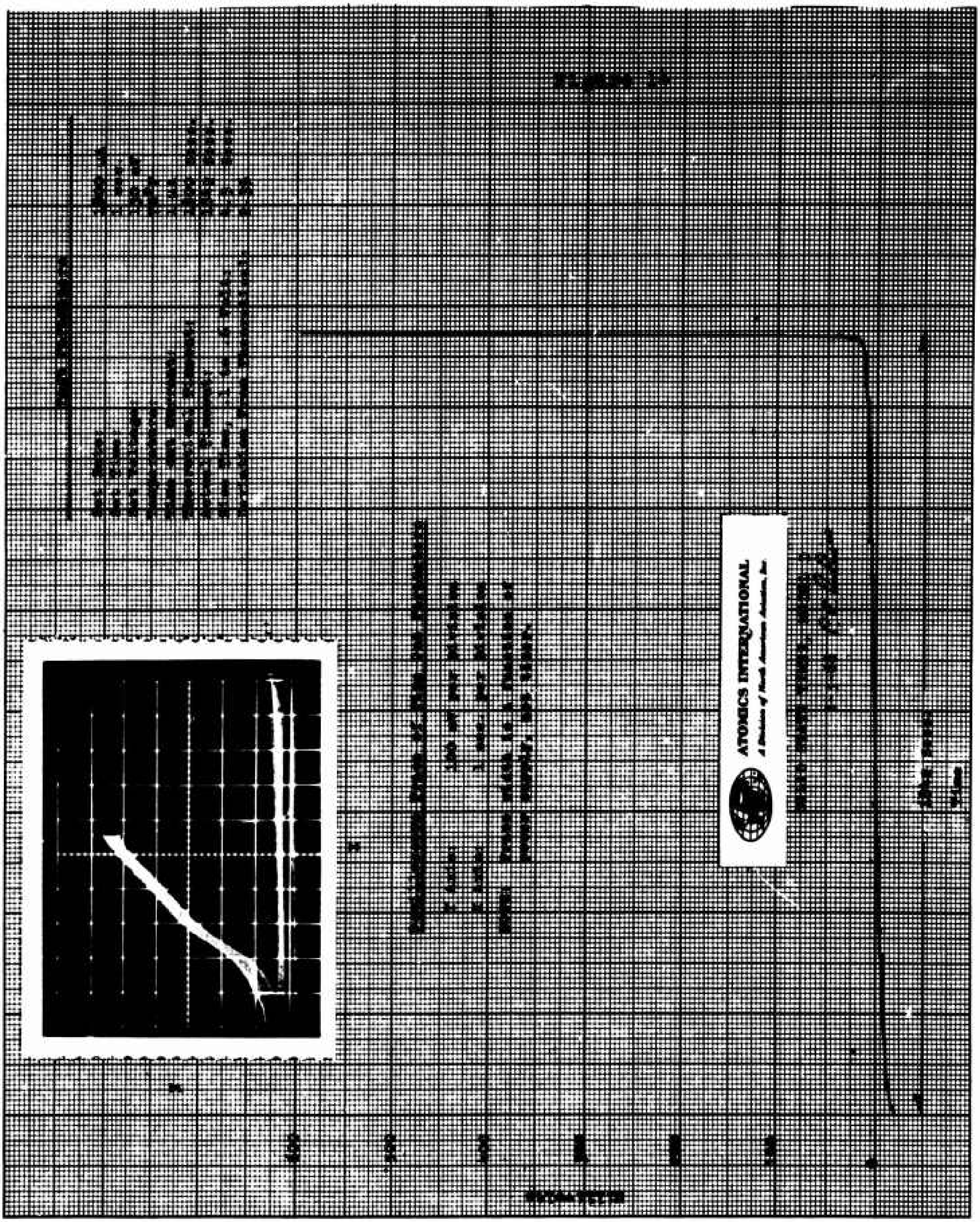
D. The limits of current for setting and operating (Fig. 13) were explored by testing over the temperature range. Figure 14 illustrates the performance of a timer when operated at 1 μA. The accuracy was good and the rise time acceptable for most circuit applications. These tests show that 3 μA and above is a safe, practical minimum operating current.

E. The fourth group of timers were fabricated with the best techniques and materials developed during the program. The performance shown in Figure 15 of these devices appears to meet the program requirements.

Serial Number 083 exhibited a malfunction at 135°F. This was due to a mechanical breakdown of the substrate and was reflected in a lower than normal stop voltage. It is therefore considered a reject although its accuracy was not effected at low temperature.

The slight variation in indicated deviation from theoretical perfect timing may be due to instrumentation error. A much more sophisticated electronic system will be required to evaluate the timing accuracy of these devices.


5-18-65
PXD/SW
-65°F
70°F
165°F
1000 µA
1500 µA
-65°F
0°F
70°F
165°F
Millivolts
Millivolts
450
400
350
300
250
200
150
100
50
0
100
75
50
25
0
1 µA
10 µA
100 µA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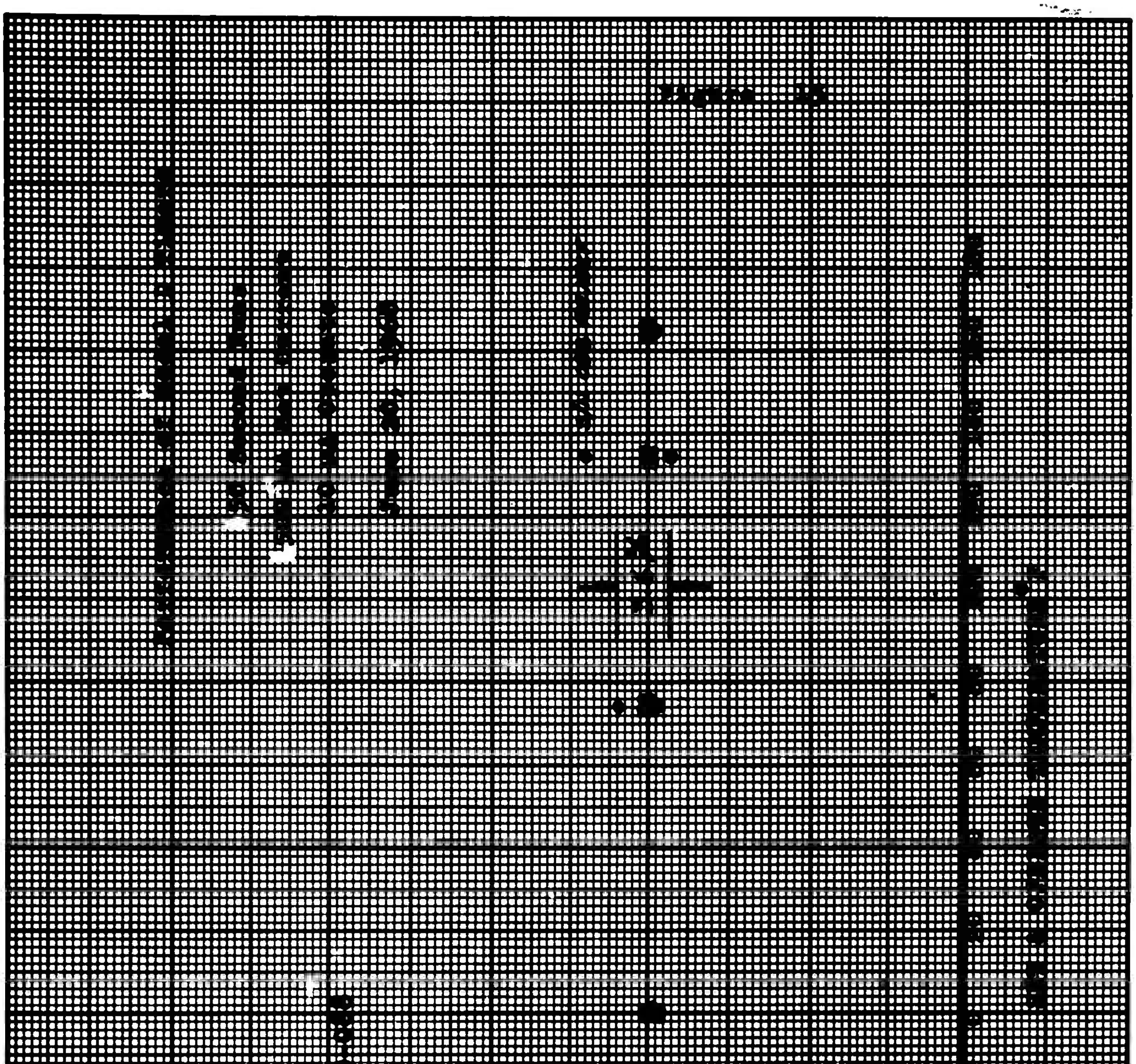

IV. CONCLUSIONS

It appears that not only has the "required" performance been met but that the "desired" performance can also be met. The data indicates that the control system for setting and operating current may limit the indicated device accuracy. If the setting time can be extended, the effect of variation of setting current on indicated accuracy can be reduced. Many more tests of many timers would be required to develop a statistical analysis of the ultimate performance of this device.

A. Modes of Failure

The performance of the device will degrade if it is held at stop voltage (.68V) after time out. If this is done the voltage drop will remain at .68 for some time. This .68V plateau is produced by a chemical reaction within the device. It has been hypotesized that if, after misusing the device in this manner, it is recycled, the device may be repaired or "healed" by repetitive operations. Cycles will short time at first. A timer was held at .68V for four hours after timing out at 10 μA. After approximately 50 cycles including some storage in the set condition, the timer returned to its normal operating mode. The analysis of this data confirms the hypothesis that the chemical reaction produced at stop voltage is reversable, i.e., the device was subject to 40 μA-hr at stop voltage; operating cycles which totaled approximately 40 μA-hr were required to heal the timer.

The melting point temperature of the electrolyte used in this device is approximately 375°F. This does not appear to impose restriction as most electronic circuit applications will not withstand this high a temperature. The device has been tested in the 200°F range and exhibits good operating efficiency. The electrolyte "flips" to a high resistance state at approximately -250°F below zero. This does not impose a problem under normal circuit conditions. The failure mode under normal operating conditions has not been identified. Recycling the device under normal conditions does not apparently reduce

the efficiency. It is interesting to note that a newly manufactured device performs more accurately after recycling a few times. Cycling a device over 100 times has not degraded its performance.

B. Capacitance of the Timer

The timer acts as a capacitor and follows the engineering design rules of a polar type capacitor. The device has a capacitance of approximately 0.5 μF. It is this capacitance that determines the lowest value for rise time attainable at any given current. However, use as a capacitor is limited by the devices high ohmic and faradaic impedance.

C. Pulse Operation of the Timer

There is no reason why the current cannot be pulsed to the timer for either setting or operating. The timer is an electrochemical device; the plating and stripping action during setting and operating is a function of the integrated current applied. The pulsed current must be within the limits specified for continuo s operation i.e., 4 μA to 1.5 mA. There does not appear to be any reason why millisecond pulses will not operate the timer as well as continuously applied currents.

D. Repeatability of the Time Cycle

Although the timers performed in the 95% to 105% accuracy range, one problem was noted that may need some consideration when designing an associated circuit.

During long storage and/or temperature changes the timer may show a partial set due to previous short cycling, i.e., if a previous cycle was 99% of theoretical, the 1% residual may affect a later timing cycle. This phenomena will not appreciably affect long term timing but might be detrimental to short term (10 seconds or less) cycles. This problem can be solved by designing a clearing feature into the associated setting circuit.

No self-setting problems were encountered even after multi hour, 200°F storage of the timers. Measurement of impurity currents also indicated that self-setting or self-operating does not occur in these devices.

E. Follow-on Studies

Although significant progress has been made in this four month program, reliability and application data should now be more fully developed.

1. Performance

This device concept is performing well but the effects of extended storage on performance, the setting and operating current and time limitations, and the operating temperature limits have not been completely defined by this limited development program. These data should be developed to provide the circuit designer with the broadest performance limits possible. This will require fabrication of devices to provide statistical numbers after exposure to temperature cycling, shock and vibration, humidity and salt fog environments, storage at various temperatures, and current-time evaluation tests.

2. Materials

Various design configurations and combinations of electrolytes, anodes, and cathodes are available which have not been completely evaluated. The most promising concepts should be assembled into timers and evaluated as described in paragraph E.1.

3. Circuit Application

The timer should be life cycled in various types of circuits to provide further information on its application to fuzes. Typical circuits should be breadboarded, and samples of each circuit evaluated for performance over the temperature range. Setting techniques, such as capacitor discharge, should also be investigated.

4. Manufacturing Analysis

A study of the present configuration should be conducted in order to provide cost effectiveness data. This should include evaluation of automated tooling with qualified suppliers, metal and ceramic parts subcontractors, and scale-up production studies of chemical preparation and handling.

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13. ABSTRACT

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3 to 1500 uA-sec	Operating Time	3 to 2000 uA-sec
10 to 100 uA	Operating Current	1 to 1500 uA
0.5 second or less	Rise Time	0.2 to 0.5 seconds
± 5% reqd. ±2-1/2 desired	Accuracy	Less than ± 2-1/2%

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